

11

Atoms in Electric and Magnetic Fields

11.1 Introduction

We shall study in this chapter mainly the effect of electric and magnetic fields on the atomic energy levels. It will be seen that when an atom is placed in a uniform magnetic field, there is *the splitting of the energy levels of an atom and hence of the associated spectral lines*. This phenomenon is known as the ***Zeeman effect***. It provides a strong experimental confirmation of the quantization of angular momentum of electron. It is interesting to note that the introduction of the concept of *spin angular momentum of electron* or *electron spin* was needed to explain, among some other phenomena, the co-called ***anomalous Zeeman effect***. We shall also study the effect of external electric field on atomic states, the so-called ***Stark effect*** where also the atomic energy levels are shifted producing a splitting of spectral lines. The Stark effect would be studied only qualitatively. We shall first recapitulate some of the matters already learnt and also introduce some others to follow the subject matter of the present chapter rather easily.

11.2 Quantum numbers

The time-independent Schrödinger equation for H-atom contains *three* independent variables. As a result, there emerges *three* quantum numbers n, l and m_l and their values are given as under:

$$n = 1, 2, 3, \dots,$$

$$l = 0, 1, 2, \dots, (n - 1)$$

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

The quantum number n , termed *principal quantum number*, is an integer that can take up values $1, 2, 3, \dots, \infty$. It arises from quantization of energy of the electron and specifies the total energy of H-atom.

The quantum number l , called *orbital quantum number* or *angular momentum quantum number*, is also an integer that can, for a given n , take up values $0, 1, 2, \dots, (n - 1)$. It is related to the magnitude of the orbital angular momentum L of the electron as:

$$L = \sqrt{l(l + 1)} \hbar \quad (11.2.1)$$

The quantum number m_l , called *magnetic quantum number*, has for a given l , $(2l + 1)$ -integral values from $-l$ to $+l$, through 0, in steps of unity.

$$\therefore m_l = l, l - 1, \dots, 2, 1, 0, -1, -2, \dots, -(l - 1), -l$$

It arises from quantization of the direction of electron's orbital angular momentum which can take up $(2l + 1)$ different directions.

• If the atom is placed in a magnetic field, the *energy of interaction* depends on the m_l -value and this justifies its nomenclature as *magnetic quantum number*.

11.3 Orbital angular momentum of electron: Vector atom model and space quantization

Classically, the orbital angular momentum \vec{L} is defined by

$$\vec{L} = \vec{r} \times \vec{p}$$

where \vec{r} is the position vector and \vec{p} the linear momentum of the particle (electron)

We are already familiar with the operator for the components of \vec{L} . The application of quantum mechanical concepts provides the following eigenvalue equations.

$$L^2 Y_{lm_l}(\theta, \phi) = l(l + 1) \hbar^2 Y_{lm_l}(\theta, \phi), \quad l = 0, 1, 2, \dots \quad (11.3.1)$$

$$L_z Y_{lm_l}(\theta, \phi) = m_l \hbar Y_{lm_l}(\theta, \phi), \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l \quad (11.3.2)$$

where $l(l + 1) \hbar^2$ is the eigenvalue of the operator \hat{L}^2 and $m_l \hbar$ is that of the operator \hat{L}_z .

The length of the angular momentum vector $|\vec{L}|$ is

$$|\vec{L}| = \sqrt{l(l+1)}h, \quad l = 0, 1, 2, \dots \quad (11.3.3)$$

and the values of $|\vec{L}|$ constitute the magnitude of the angular momentum of electron.

• Note that these values are strikingly different from what we had in Bohr model where the electron in the n th orbit had an angular momentum $nh/2\pi$ or nh . In quantum mechanical model, the electron in the state n has values $l = 0, 1, 2, \dots, (n-1)$ and the greatest value of angular momentum corresponds to $l = n-1$ and hence is given by $\sqrt{n(n-1)}h$. Thus, *the angular momentum of electron in Bohr model is always greater than the highest value given by quantum mechanics.*

We may now summarise the behaviour of *quantum mechanical angular momentum*. We note that when $m = +l$ or $m = -l$, so that the orbital angular momentum are respectively *parallel* and *anti-parallel* to the z -axis, its x - and y -components are still not zero, but their average values are always zero, i.e., $\langle L_x \rangle = 0$ and $\langle L_y \rangle = 0$. The maximum value of the component of \vec{L} on the z -axis is lh i.e., less than the magnitude of \vec{L} which is $\sqrt{l(l+1)}h$. These results are conveniently visualised pictorially in terms of a model, called the *vector model* of angular momentum.

According to this model, the vector \vec{L} precesses about the z -axis such that its projections on this axis is constant. This property is often called *space quantization*. The magnitude of \vec{L} is $\sqrt{l(l+1)}h$ and its projection L_z on z -axis is *quantized*, the

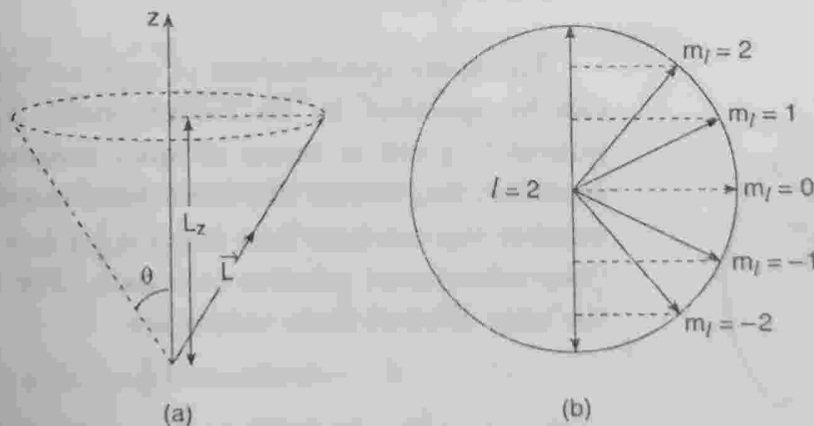


Fig. 11.1 (a) Precession of \vec{L} about z -axis, (b) Possible orientations of \vec{L} for $l=2$

allowed values of L_z being $m_l h$, $m_l = -l, -l+1, \dots, 0 \dots l-1, +l$, i.e., $(2l+1)$ values in all. Thus the vector \vec{L} may be viewed as lying on the surface of a cone with altitude $m_l h$, semi-vertical angle θ , and the z -axis as its *axis of symmetry*; all orientations of \vec{L} on the surface of the cone are equally likely (Fig. 11.1a). The possible orientations of \vec{L} for $L = 2$ are shown in Fig. 11.1b. The angle θ between the z -axis and vector \vec{L} is given by

$$\cos \theta = \frac{L_z}{|\vec{L}|} = \frac{m_l h}{\sqrt{l(l+1)}h} = \frac{m_l}{\sqrt{l(l+1)}} \quad (11.3.4)$$

This peculiar behaviour of angular momentum in quantum mechanics is in accord with the *uncertainty principle*. If \vec{L} were fixed in space, all its components L_x, L_y and L_z had definite values and the particle would have to be in a definite plane all the times. This would violate the uncertainty principle. For instance, if \vec{L} points always to the z -direction, the electron would be in xy -plane all the time. Since the z -coordinate is fixed ($z = 0$), the z -component p_z of its momentum will have infinite uncertainty according to the uncertainty principle, which is impossible.

11.4 Spin angular momentum or spin of electron

The idea of spinning electron was first introduced by Uhlenbeck and Goudsmit (1925) to explain the *multiplet structure* (fine structure) of spectral lines. They proposed that an electron in an atom must have an *intrinsic angular momentum* (eigen angular momentum) of value $\frac{1}{2}\hbar$ in addition to and independent of its orbital angular momentum. This intrinsic angular momentum \vec{S} is called *spin angular momentum vector* or simply *spin* of the electron and is specified by the *spin quantum number*, $s = \frac{1}{2}$.

They also proposed that spin angular momentum vector \vec{S} is very similar to that of orbital angular momentum \vec{L} . The magnitude of \vec{S} is thus

$$|\vec{S}| = \sqrt{s(s+1)}\hbar = \sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)}\hbar = \sqrt{3}\hbar/2 \quad (11.4.1)$$

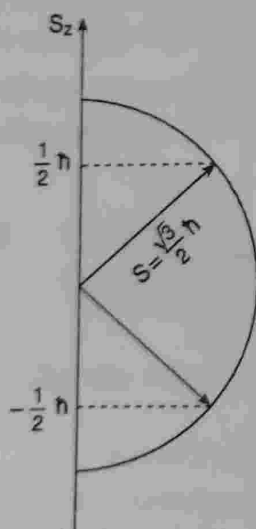


Fig. 11.2 Two possible orientations of spin angular momentum relative to z -axis

The space quantization of spin angular momentum can be specified by its z -component S_z . This component is given in terms of *spin magnetic quantum number*, m_s , which, like the orbital magnetic quantum number m_l , can have $2s+1 = 2 \times \frac{1}{2} + 1 = 2$ orientations (two-valuedness) relative to z -axis. For m_s , therefore, the only allowed state values are

$$m_s = \pm \frac{1}{2} \quad (11.4.2)$$

as shown in Fig. 11.2. The z -component of spin angular momentum is thus

$$S_z = m_s \hbar = \pm \frac{1}{2} \hbar \quad (11.4.3)$$

$S_z = \pm \frac{1}{2} \hbar$ is called '*spin-up*' position and $S_z = -\frac{1}{2} \hbar$, the '*spin-down*' position.

• Do not please get trapped of visualizing the spinning electron as a case of spinning about its own axis like a spinning top. Such a classical depiction is simply wrong. In fact, it is *purely* a quantum mechanical attribute having no classical parallel! A free electron has no orbital angular momentum, but all electrons, free or bound, in

atoms have the same spin. We cannot describe electron spin as any kind of motion in space-time. It is a *two-valuedness* that has an *in born* tendency to behave as angular momentum. *Spin is one more strangeness of the quantum world!* It must be accommodated. In 1928 Dirac in his relativistic quantum mechanics showed that the concept of spin appears naturally.

• Spin is associated not only with electrons but with all particles in nature. The particles having $s = 0, 1, 2, 3, \dots$ etc., i.e., integrals are called *bosons* and those having $s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$ etc., i.e., half-integrals are called *fermions*.

It thus turns out that for a complete description of the state of an electron in an atom, as many as four quantum numbers, n, l, m_l and m_s are required. The existence of the fourth quantum number m_s , over and above n, l, m_l , was first suggested by Pauli in 1920 without, however, any explanation of its significance. This was followed, in 1922, by Stern-Gerlach's experiment. They demonstrated convincingly the existence of another angular momentum (spin angular momentum) in addition to the orbital one.

11.5 Total angular momentum of electron

We shall consider hydrogen or hydrogen-like atoms with one electron moving around the nucleus.

The electron has both orbital angular momentum \vec{L} and the spin angular momentum \vec{S} . The magnitude of \vec{L} is

$$L = \sqrt{l(l+1)} \hbar \quad (11.5.1)$$

where l is the orbital angular momentum quantum number.

The component of \vec{L} along the z -axis is

$$L_z = m_l \hbar \quad (11.5.2)$$

where m_l is the orbital magnetic quantum number.

Similarly, the magnitude of \vec{S} is given by

$$S = \sqrt{s(s+1)} \hbar \quad (11.5.3)$$

where s is the spin quantum number having the value $\frac{1}{2}$.

The z -component of \vec{S} is given by

$$S_z = m_s \hbar \quad (11.5.4)$$

where m_s is the spin magnetic quantum number which have values $\pm \frac{1}{2}$.

The total angular momentum vector \vec{J} of electron is the vector sum of \vec{L} and \vec{S}

$$\therefore \vec{J} = \vec{L} + \vec{S} \quad (11.5.5)$$

The magnitude of \vec{J} , like those of \vec{L} and \vec{S} , is given by

$$J = |\vec{J}| = \sqrt{j(j+1)} \hbar \quad (11.5.6)$$

where $j = l + s$ or $|l - s|$ and is called the *total angular momentum quantum number*.

Obviously, j is always half an odd integer. In case $l = 0$, j can have only the value $\frac{1}{2}$. If $l = 1$, $j = 1 \pm \frac{1}{2}$, i.e., $3/2$ or $1/2$. If $l = 2$, $j = 2 \pm \frac{1}{2}$ i.e., $5/2$ or $3/2$ and so on and so forth.

The possible values of the component of \vec{J} along the z -axis may be written in analogy with components of L_z and S_z as

$$J_z = m_j h \quad (11.5.7)$$

$$\text{where } m_j = m_l \pm m_s \quad (11.5.8)$$

For a given value of j , m_j can take up $(2j+1)$ -values, from $-j$ to $+j$, in steps of unity.

$$\therefore m_j = -j, -j+1, \dots, (j-1), j \quad (11.5.9)$$

For a one-electron atom, therefore, the possible values of j are $l + \frac{1}{2}$ and $|l - \frac{1}{2}|$.

While the former corresponds to \vec{L} and \vec{S} having parallel z -components, the latter to \vec{L} and \vec{S} having anti-parallel z -components. The two possible ways of combining \vec{L} and \vec{S} to form \vec{J} (i.e., either parallel or antiparallel) is shown in Fig. 11.3. It is to be kept in mind that \vec{L} and \vec{S} can never be parallel or anti-parallel to each other or to \vec{J} .

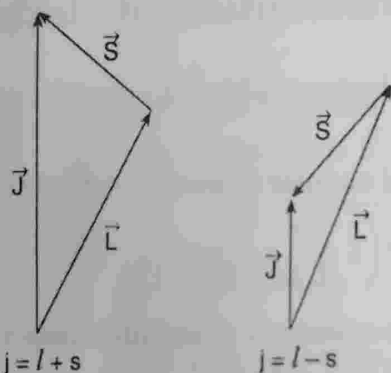


Fig. 11.3 Two ways (parallel and antiparallel) of combining \vec{L} and \vec{S} to form \vec{J}

Since both \vec{L} and \vec{S} show space quantization, \vec{J} will also expectedly show space quantization. The spin and orbital motion produce *internal magnetic fields*. This causes the vector \vec{L} and \vec{S} to exert torques on each other. The effect of the torques is to make \vec{L} and \vec{S} precess about their resultant \vec{J} whose magnitude and direction are conserved in absence of an external magnetic field. This is illustrated in Fig. 11.4a.

In an external field \vec{B} , (assumed to be along z -axis), \vec{J} precesses about the z -axis as shown in Fig. 11.4b. The precession of \vec{L} and \vec{S} about the precessing \vec{J} is rather very complicated.

Angle between \vec{L} and \vec{S} —We have $\vec{J} = \vec{L} + \vec{S}$.

$$\Rightarrow J^2 = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) = L^2 + S^2 + 2\vec{L} \cdot \vec{S}$$

$$= L^2 + S^2 + 2LS \cos \theta$$

$$\therefore \cos \theta = \frac{J^2 - L^2 - S^2}{2LS} \quad (11.5.10)$$

where θ is the angle between the vectors \vec{L} and \vec{S} .

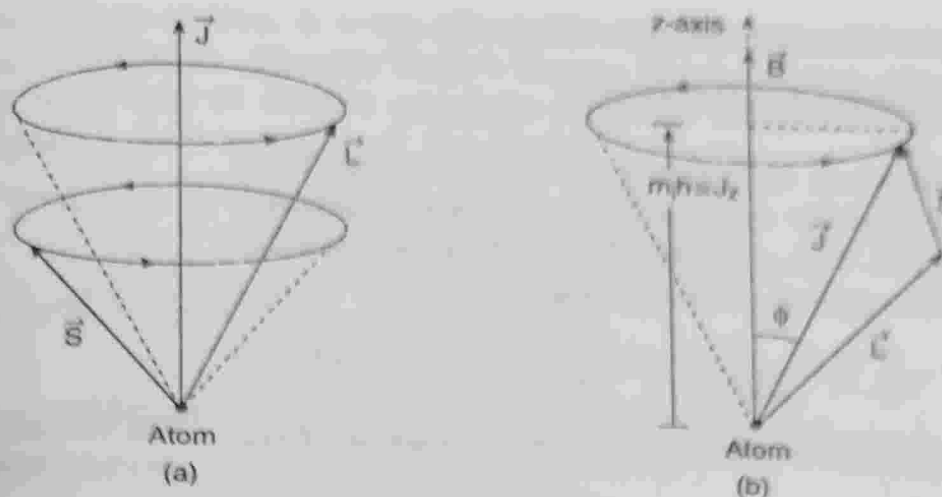


Fig. 11.4 (a) Precession of \vec{L} and \vec{S} about \vec{J} and (b) Precession of \vec{J} about the external magnetic field \vec{B} along the z-axis

Now since $J^2 = j(j+1)\hbar^2$, $L^2 = l(l+1)\hbar^2$ and $S^2 = s(s+1)\hbar^2$

$$\cos \theta = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)} \cdot \sqrt{s(s+1)}} \quad (11.5.11)$$

Angle between \vec{J} and the z-axis—If ϕ be the angle between \vec{J} and the z-axis,

$$\cos \phi = \frac{J_z}{J} = \frac{m_j \hbar}{\sqrt{j(j+1)}\hbar} = \frac{m_j}{\sqrt{j(j+1)}} \quad (11.5.12)$$

The maximum value of m_j is j which is less than $\sqrt{j(j+1)}$. It thus follows from (11.5.12) that \vec{J} can never align itself along the z-axis.

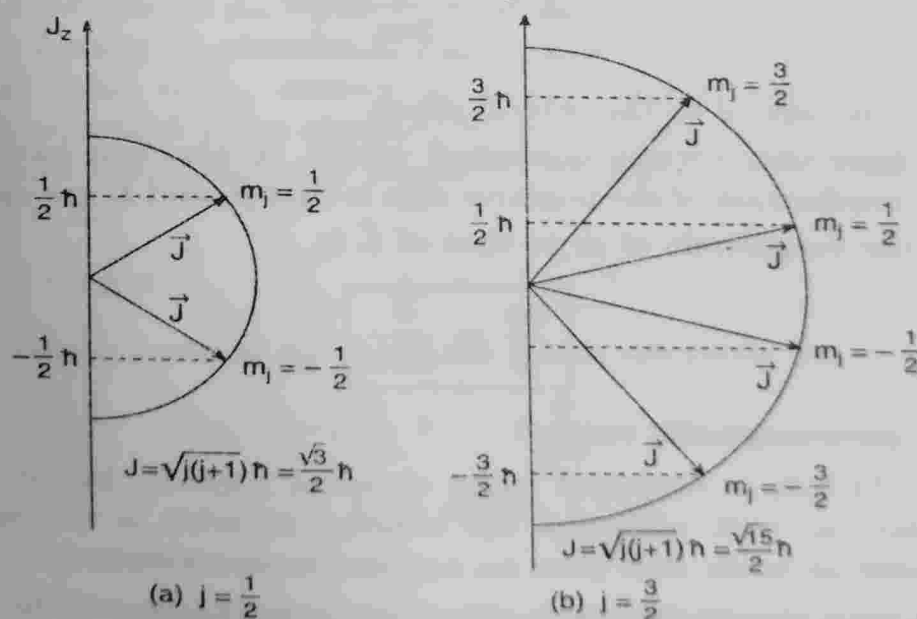


Fig. 11.5 Space quantization of total angular momentum when $l=1$ for two j -states

The possible orientations of vector \vec{J} with respect to z-axis for different j -states that correspond to $l=1$ are illustrated in Fig. 11.5.

11.6 Magnetic moment due to an orbiting electron

An electron of charge $-e$ circulating the nucleus (Fig. 11.6) is equivalent to a circular current loop and hence behaves as a *magnetic dipole*. The current i in the loop is the ratio of the charge to the period of revolution T .

$$\therefore i = -\frac{e}{T} = -\frac{e}{2\pi r/v} = -\frac{ev}{2\pi r} \quad (11.6.1)$$

where v is the speed of the electron and r the radius of the electron-orbit.

It would give rise to a magnetic *dipole moment* μ_l given by

$$\begin{aligned} \mu_l &= \text{current} \times \text{area of loop} \\ &= iA = -\frac{ev}{2\pi r} \pi r^2 \\ &= -\frac{e}{2m} mvr = -\frac{e}{2m} L \end{aligned} \quad (11.6.2)$$

where $L = mvr = mr^2\omega$, the magnitude of the *orbital angular momentum*, ω = the angular velocity.

But the magnetic moment $\vec{\mu}_l$ and the angular momentum \vec{L} are both vectors. So,

$$\boxed{\vec{\mu}_l = -\frac{e}{2m} \vec{L}} \quad (11.6.3)$$

\vec{L} is always directed normal to the orbital plane.

Since \vec{L} can have only certain quantized values, $\vec{\mu}_l$ also can have certain allowed values only. The implication of the negative sign is that $\vec{\mu}_l$ and \vec{L} are *oppositely directed*.

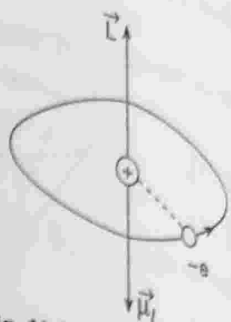
The ratio of the magnitude of $\vec{\mu}_l$ to that of \vec{L} is

$$\boxed{\frac{\mu_l}{L} = \frac{e}{2m}} \quad (11.6.4)$$

and is called the *gyromagnetic ratio*.

● Expression (11.6.3) is obtained using classical physics, but it remains true in quantum mechanics as well, although the concept of orbit is not valid in quantum mechanics. A quantum state *does* have an angular momentum.

● In multi-electron atoms, the total orbital magnetic moment is the algebraic sum of the magnetic moments of individual electrons. *The magnetic moment of a completely filled shell is zero*, so that only the partially filled shells will give a non-zero orbital magnetic moment.



According to Bohr's theory, $L = n\hbar$, $n = 1, 2, 3, \dots$. For the ground state, $n = 1$ and from (11.5.3) $\mu_l = (e/2m)\hbar$. Though Bohr's theory is not correct, this quantity serves as a convenient basic unit of atomic magnetic moment. It is called *Bohr magneton*, symbolized by μ_B .

$$\mu_B = \frac{e\hbar}{2m} = \frac{e\hbar}{4\pi m} \quad (11.6.5)$$

Its magnitude is 9.274×10^{-24} J/T or A.m².

11.7 Magnetic moment due to electron spin

We have seen that an atom possesses a magnetic moment due to the orbital angular momentum of its electron and is given by

$$\vec{\mu}_L = -\frac{e}{2m}\vec{L} \quad (11.7.1)$$

We may assume, by extrapolation, that there exists an atomic magnetic moment due to its spin angular momentum as well. And it is proved to be correct. The magnetic moment due to spin however is given by

$$\vec{\mu}_S = -g_s \frac{e}{2m}\vec{S} \quad (11.7.2)$$

where \vec{S} is the spin angular momentum.

The presence of the factor g_s , which does not appear in (11.7.1), is purely, a quantum mechanical factor having no classical analogue. It is called *spin gyromagnetic ratio*. The experimental value of g_s , correct up to six decimal places, is 2.000231 which agrees with the theoretical value obtained from quantum electrodynamics. In Dirac's relativistic quantum mechanics, the magnetic moment due to electron spin emerges naturally with $g_s = 2$.

Taking $g_s = 2$, we get

$$\vec{\mu}_S = -2\frac{e}{2m}\vec{S} \quad (11.7.3)$$

The possible components of $\vec{\mu}_S$ along the z-axis are given by

$$\mu_{S_z} = -2\frac{e}{2m}S_z = \pm \frac{e\hbar}{2m} = \pm 1\mu_B$$

$$\left(\because S_z = m_s\hbar = \pm \frac{1}{2}\hbar \right)$$

where μ_B is Bohr magneton.

• It is interesting to note that while for the magnetic moment due to orbital angular momentum, the proportionality constant between the two is $e/2m$, that due to spin has double the value; g_s for spin is 2. The spin thus contributes double the magnetism of orbital motion!

11.8 Larmor precession

If a dipole of magnetic moment $\vec{\mu}_l$ is placed in an external magnetic field \vec{B} , it acquires a potential energy $V = -\vec{\mu}_l \cdot \vec{B}$. By classical electromagnetism, it experiences a torque

$$\vec{\tau} = \vec{\mu}_l \times \vec{B} \quad (11.8.1)$$

The role of the torque is to align the dipole in the field direction. As $\vec{\mu}_l$ and \vec{L} are oriented antiparallel, $\vec{\tau}$ would be perpendicular to $\vec{\mu}_l$, \vec{L} and \vec{B} . But, we have from mechanics,

$$\vec{\tau} = d\vec{L}/dt \quad (11.8.2)$$

So, $d\vec{L}/dt$ is also perpendicular to $\vec{\mu}_l$, \vec{L} and \vec{B} , implying that $d\vec{L}$, the change in angular momentum, is in the direction of $\vec{\tau}$. Since the magnitude of \vec{L} vector remains the same, its direction must undergo change to produce change in \vec{L} . Thus, the change in angular momentum $d\vec{L}$ requires the **precession** of \vec{L} about the magnetic field \vec{B} , as shown in Fig. 11.7. Since $\vec{\mu}_l$ and \vec{L} are antiparallel, both $\vec{\mu}_l$ and \vec{L} precess about the magnetic field. This precession is known as **Larmor precession** and the frequency of precession is termed **Larmor angular frequency**, ω_L .

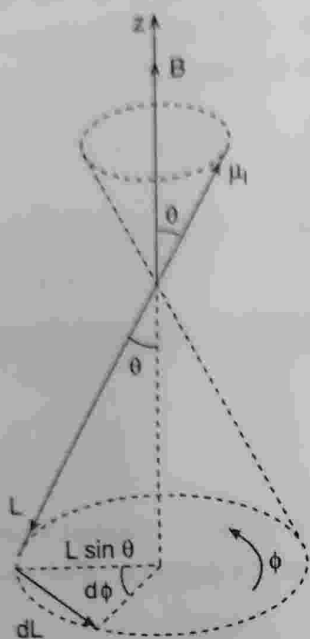


Fig. 11.7 Precessional motion of a magnetic dipole of moment $\vec{\mu}_l$ placed in an external magnetic field \vec{B} . The vectors $\vec{\mu}_l$ and \vec{L} are antiparallel

$$\begin{aligned} \text{Now, } \omega_L &= \frac{d\phi}{dt} = \frac{1}{L \sin \theta} \cdot \frac{dL}{dt}, \text{ from Fig. 11.7} \\ &= \frac{1}{L \sin \theta} \tau = \frac{\mu_l B \sin \theta}{L \sin \theta} = \frac{\mu_l B}{L}, \end{aligned} \quad (11.8.3)$$

using equations (11.8.2) and (11.8.1)

Substituting for L from (11.6.2), we obtain

$$\begin{aligned} |\omega_L| &= \frac{e}{2m\mu_l} \cdot \mu_l B \\ &= \frac{eB}{2m} = \frac{\mu_B}{\hbar} B \end{aligned} \quad (11.8.4)$$

The **cause of precession** is this: With application of the field, $\vec{\mu}_l$ tends to align itself along \vec{B} for that corresponds to the minimum energy and this tendency of $\vec{\mu}_l$ results in rotational energy which must be dissipated. But there is no available process for energy-dissipation. So $\vec{\mu}_l$, in its tendency to align along \vec{B} precesses about \vec{B} , keeping θ and energy constant.

11.9 Total magnetic moment : Lande g -factor

The magnetic moment of an atom is due to the orbital motion and also the spin of electron. The magnetic moment due to electron's orbital motion is

$$\vec{\mu}_L = - \left(\frac{e}{2m} \right) \vec{L} \quad (11.9.1)$$

and that due to spin motion is given by

$$\vec{\mu}_S = -g_s \left(\frac{e}{2m} \right) \vec{S} = -2 \left(\frac{e}{2m} \right) \vec{S}, \text{ taking } g_s = 2 \quad (11.9.2)$$

Total magnetic moment is given by

$$\begin{aligned} \vec{\mu}_T &= \vec{\mu}_L + \vec{\mu}_S \\ &= -\frac{e}{2m} (\vec{L} + 2\vec{S}) = -\frac{e}{2m} (\vec{J} + \vec{S}) \end{aligned} \quad (11.9.3)$$

where $\vec{J} = \vec{L} + \vec{S}$, the total angular momentum vector.

Fig. 11.8 shows schematically the relationship between the angular momentum vectors and the magnetic moment vectors. The resultant magnetic moment $\vec{\mu}_T (= \vec{\mu}_L + \vec{\mu}_S)$ is not along \vec{J} . Since \vec{L} and \vec{S} precess about \vec{J} , both $\vec{\mu}_L$ and $\vec{\mu}_S$ must also precess about \vec{J} and hence also their resultant $\vec{\mu}_T$. The *effective magnetic moment* of electron will thus be $\vec{\mu}_J$, the component of $\vec{\mu}_T$ along \vec{J} . The component of $\vec{\mu}_T$ normal to \vec{J} will average out to zero in one complete revolution.

$$\therefore \vec{\mu}_J = (\vec{\mu}_T \cdot \hat{J}) \hat{J}, \quad (11.9.4)$$

\hat{J} being the *unit vector* along the vector \vec{J} , i.e., $\hat{J} = \vec{J}/J$.

$$\text{So, from (11.9.4),} \quad \vec{\mu}_J = \frac{(\vec{\mu}_T \cdot \vec{J}) \vec{J}}{J^2} \quad (11.9.5)$$

$$= -\frac{e}{2m} \left[\frac{(\vec{J} + \vec{S}) \cdot \vec{J}}{J^2} \right] \vec{J}, \quad (11.9.6)$$

using equation (11.9.3).

We shall now evaluate the quantity

$$g = (\vec{J} + \vec{S}) \cdot \vec{J} / J^2 \quad (11.9.7)$$

for a given (lsj) -state.

We have:

$$(\vec{J} + \vec{S}) \cdot \vec{J} = J^2 + \vec{S} \cdot \vec{J} \quad (11.9.8)$$

Also, since $\vec{L} = \vec{J} - \vec{S}$,

$$L^2 = J^2 + S^2 - 2\vec{S} \cdot \vec{J}$$

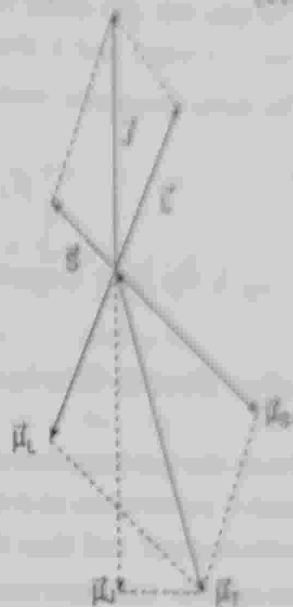


Fig. 11.8 Relationship between angular momentum vectors and magnetic moment vectors

$$\therefore \vec{S} \cdot \vec{J} = \frac{J^2 + S^2 - L^2}{2}$$

$$\therefore \text{From (11.9.8), we get } (\vec{J} + \vec{S}) \cdot \vec{J} = J^2 + \frac{J^2 + S^2 - L^2}{2}$$

Substituting (11.9.9) in (11.9.7),

$$g = 1 + \frac{J^2 + S^2 - L^2}{2J^2} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (11.9.10)$$

on replacing J^2 , L^2 and S^2 by their quantum mechanical values: $j(j+1)\hbar^2$, $l(l+1)\hbar^2$ and $s(s+1)\hbar^2$.

The quantity g is called the **Lande g -factor**. Its value plainly depends on quantum numbers l , s and j and is thus different in different states.

The **total magnetic moment**, μ_J of electron in terms of g is thus, from (11.9.6)

$$\vec{\mu}_J = -g \left(\frac{e}{2m} \right) \vec{J} = -g\mu_B \vec{J} \hbar \quad (11.9.11)$$

where μ_B is the Bohr magneton.

11.10 Stern-Gerlach experiment ✓

The Stern-Gerlach experiments (1922) were a *direct* confirmation of *space quantization of angular momentum* and the concept of *electron spin*. It is a device to measure magnetic moment and thus the angular momentum.

Set-up—In the experimental arrangement (Fig. 11.9a), a narrow beam of neutral atoms was sent from an *oven* O through *collimating slits* S and is allowed to pass through a *non-uniform magnetic field* NS directed along the z -axis to receive finally on a *collecting photographic plate* P . The non-uniform field is produced by a magnet with specially designed pole pieces; the upper pole piece is in the form of a knife edge and the lower one with a channel cut into it parallel to the knife edge. The field has thus a gradient in the z -direction. The whole arrangement is enclosed in an evacuated chamber to enable the atoms traverse the field without collision.

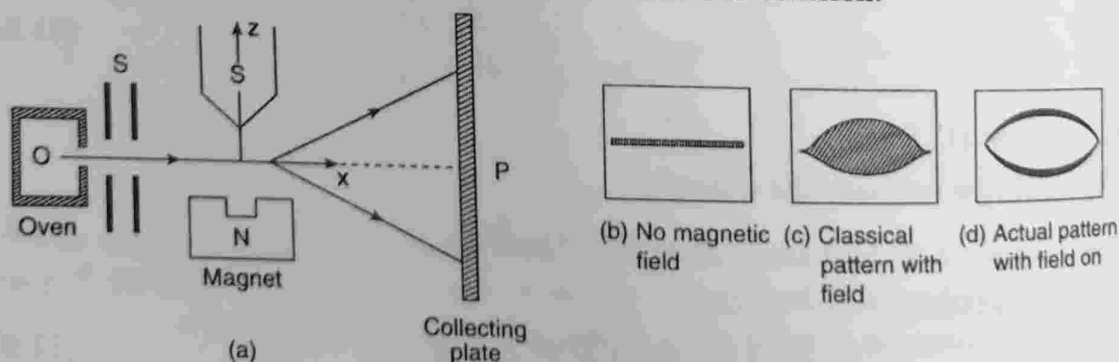


Fig. 11.9 Stern-Gerlach Experiment

With no magnetic field, the beam produces a single trace on the collecting plate (Fig. 11.9b). When the field is switched on, the trace splits distinctly into more than one trace. We shall now discuss the theory of the experiment to follow this outcome.

Theory—Ignoring spin (which was not known at the time), each atom consists of electrons with orbital angular momenta and hence magnetic moments (Art. 11.3 and Art. 11.9). If $\vec{\mu}$ be the resultant magnetic moment of the atom and \vec{B} the applied magnetic field, then the potential energy of the atom in the field is

$$V = -\vec{\mu} \cdot \vec{B} = \left(\frac{e}{2m} \right) \vec{L} \cdot \vec{B} = \frac{e}{2m} L_z B_z \quad (11.10.1)$$

where \vec{L} is the resultant orbital angular momentum of the atom and $B = B_z$.

The force on the atomic dipole is

$$F_z = -\frac{dV}{dz} = -\frac{e}{2m} L_z \frac{dB_z}{dz} \quad (11.10.2)$$

In absence of space quantization, \vec{L} vector of different atoms could point in different directions arbitrarily and L_z could take any value from $+L$ to $-L$. So, when the magnetic field is imposed, different atoms will move up or down by different amounts till they strike the plate, resulting in the spreading out of the trace (Fig. 11.9c), which however did not occur. The beam, in fact, split into a few subbeams (Fig. 11.9d), each with a well-defined separate trace on the plate. The number of traces depends on the type of atoms forming the beam. This is possible *only if the angular momentum is quantized*. For when L is quantized, then the possible values of L_z are $m_l \hbar$ where the magnetic quantum number m_l can take $(2l + 1)$ -values, from $-l$ to $+l$, l being the orbital quantum number. The beam must therefore split into $(2l + 1)$ sub-beams.

But there is a *problem*. Since $(2l + 1)$ is odd, the number of traces would always be odd. But this was not so for all types of atoms, e.g., with silver atoms with which Stern and Gerlach worked, the beam splits into *two*, an even number. The explanation came only when the hypothesis of *electron spin* was proposed by Uhlenbeck and Goudsmit, since spin would also contribute to the magnetic moment of electron. The valency of silver is one and we now know that the orbital and spin magnetic moments of all but the valence electron in a silver atom cancel. For this electron, the orbital angular momentum, and hence the orbital magnetic moment is zero. So, if spin were not there, a silver beam would not have split at all in a magnetic field!

If however *spin is taken into account*, it takes up only *two* orientations in a magnetic field corresponding to $m_s = \pm \frac{1}{2}$. Hence, there would be two subbeams as observed. Hence, Stern-Gerlach experiment was a direct confirmation of *space quantization* and the hypothesis of *electron spin*.

11.11 Spectroscopic notation for atomic states

The spectroscopic notation, also called the *term notation*, for an atomic state is symbolized by

$$^{2s+1} \mathcal{J}_j$$

where s is the resultant spin quantum number of the atom, j the total angular momentum quantum number and the symbol \mathcal{J} denotes the letter corresponding to the orbital angular momentum quantum number l by the scheme given below.

l -value	:	0	1	2	3	4	5	...
Letter \mathcal{J}	:	S	P	D	F	G	H	...

The superscript $2s + 1$ is known as the *multiplicity of the state*.

In case of one-electron atoms or atoms with a single valence electron (e.g., sodium), the principal quantum number n of this electron is often attached as a prefix to the term symbols, i.e.,

$$n^{2s+1} \mathcal{J}_j$$

For instance, the *ground state of hydrogen* atom has $n = 1$, $l = 0$ and is therefore symbolized by

$$1^2S_{1/2} \quad \text{or simply } ^2S_{1/2}$$

The *ground state of sodium* has $n = 3$, $l = 0$

$$\therefore \text{Term symbol is } 3^2S_{1/2} \quad \text{or simply } ^2S_{1/2}$$

The P -states of a one-electron atom are denoted by

$$^2P_{1/2}, \quad ^2P_{3/2}$$

The D and F states are similarly denoted respectively by

$$^2D_{3/2}, \quad ^2D_{5/2}$$

$$\text{and } ^2F_{5/2}, \quad ^2F_{7/2}.$$

• Note that the S -state is always a *singlet* but the term notation shows that it is a doublet. The multiplicity is $2s + 1$ only when $l > s$ and is $2l + 1$ when $s > l$.

11.12 Zeeman effect

The *Zeeman effect* is the phenomenon of *splitting of atomic energy levels and consequently of the associated spectral lines when the atoms are placed in an external magnetic field*. This was first experimentally observed (1896) by Peter Zeeman who found that many spectral lines were split into groups of closely spaced lines.

Lorentz gave an explanation of the splitting of lines based on classical physics which we shall not discuss. According to Lorentz theory, a spectral line must split into *three components—one of the same frequency as the original line and the two others have frequencies higher and lower than the original frequency by the same amount*. Experimentally also, this was observed in the spectra of some elements under certain conditions. This is called the *normal Zeeman effect*.

However, in more general cases, the splittings are complex and a line is split into *more than three components—four, six and even more—* and even when only three

components are present, their spacing does not always agree with the prediction of the classical theory. It was therefore known as *anomalous Zeeman effect*, although there is no anomaly in it. However, the name still persists.

A complete understanding of the Zeeman effect was possible *quantum mechanically*, only after the concept of *electron spin* was introduced. The normal Zeeman effect however can be explained if we ignore spin and consider only the orbital motion of the electron. We shall do this in the following sections. But why an external magnetic field will at all affect the atomic energy levels? This is due to the fact that both the orbital and spin motion of electron lead to magnetic moments and they interact with the external magnetic field.

• Zeeman effect provides a strong experimental confirmation of quantization of angular momentum and also explains why m_l is called *magnetic quantum number*.

11.12.1 Experimental set-up

The experimental set-up for the production and demonstration of Zeeman effect is shown in Fig. 11.10. S is the source emitting line spectrum such as a mercury arc or helium discharge tube and P_1 and P_2 are the pole pieces of an electromagnet between which S is placed. For making longitudinal observations possible, one of the pole pieces

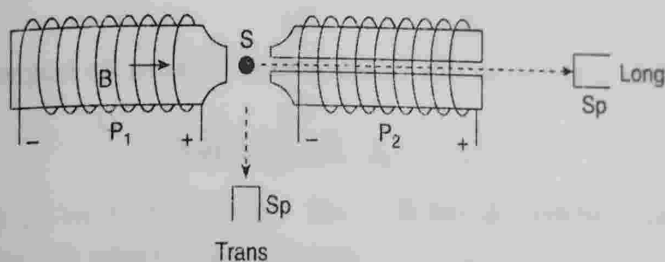


Fig. 11.10 Experimental set up for Zeeman effect

P_2 is bored to allow the light to pass through and fall on a high resolution spectrograph (Sp) for photographic record of the Zeeman lines.

Observations—When the source of light S is placed in the magnetic field, the spectral line undergoes the following striking modifications (Fig. 11.11)

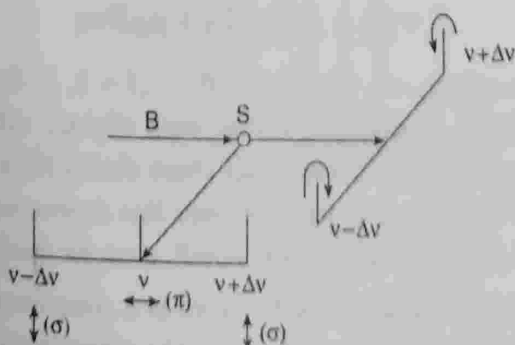


Fig. 11.11 Normal Zeeman effect : Longitudinal and transverse views

1. When the spectral line or frequency ν is examined *parallel* to the magnetic field (*longitudinal view*), each line appears to split into *two*, on the opposite sides of and equidistant from, the original line. The lines, having frequencies $\nu \pm \Delta\nu$, are *circularly polarized* in opposite sense, the higher frequency line is along the direction of the magnetising current.

2. When observed *perpendicular* to the magnetic field (*transverse view*), each spectral line splits into *three* lines or triplet, the central line appearing in the same position as the original line of frequency ν . It is *plane polarized* with vibrations *parallel* to the magnetic field and is called the π -component. The two outer components, called the σ -components, are symmetrical about the central line and are *plane polarized* with vibrations *perpendicular* to the field. Their frequencies have the same values as in the longitudinal view: $\nu \pm \Delta\nu$.

• The experimental set-up for *anomalous Zeeman effect* is identical with that of normal Zeeman effect. In anomalous Zeeman effect, only the splitting of spectral lines is more than those of the normal effect.

11.13 Theory (Explanation) of normal Zeeman effect

Let an atom, having only orbital angular momentum \vec{L} , be placed in an external magnetic field \vec{B} along the z -axis and its quantum state be specified by the orbital quantum number l and energy E_0 .

The energy ΔE of the atom due to *interaction* between its magnetic moment and the field is

$$\Delta E = -\vec{\mu}_l \cdot \vec{B} = \mu_l B \cos \theta \quad (11.13.1)$$

where θ is the angle between \vec{L} and \vec{B} .

Now, since
$$\vec{\mu}_l = -\frac{e}{2m} \vec{L} \quad \text{and} \quad \cos \theta = \frac{L_z}{L} = \frac{m_l \hbar}{L}, \quad (11.13.2)$$

$$\Delta E = \frac{eLB}{2m} \cdot \frac{m_l \hbar}{L} = \frac{e\hbar}{2m} B m_l = \mu_B B m_l,$$

using (11.13.1) and (11.13.2), where $\mu_B = e\hbar/2m =$ Bohr magneton.

Thus, the energy of the state E is given by

$$E = E_0 + \Delta E = E_0 + \mu_B B m_l \quad (11.13.3)$$

But m_l has $(2l + 1)$ -values, $-l, -l + 1, \dots, 0, \dots, l - 1, l$. So, an energy level with a particular l contains $(2l + 1)$ different states, each slightly different and determined by m_l . When no magnetic field is present, all these states have the same energy, i.e., they are *degenerate* and the *magnetic field removes this degeneracy*. The adjacent levels differ in energy by $\mu_B B$, which is rather very small, even for fairly high magnetic fields.

Because of the splitting of energy levels, there is a consequent splitting of spectral lines as well. But every line splits into *three*, as the transitions between the states of

different l -values are controlled by the so-called *selection rules*:

$$\Delta l = \pm 1,$$

$$\Delta m_l = 0, \pm 1$$

Frequency shift—Considering the transitions between the initial and the final energy levels E_i and E_f , we get

$$E_i = (E_0)_i + \mu_B B (m_l)_i \quad (11.13.4)$$

$$E_f = (E_0)_f + \mu_B B (m_l)_f \quad (11.13.5)$$

$$\Rightarrow E_i - E_f = (E_0)_i - (E_0)_f + \mu_B B \Delta m_l$$

$$\text{or, } h\nu = h\nu_0 + \mu_B B \Delta m_l. \quad (11.13.6)$$

$$\therefore \nu = \nu_0 + \frac{eB}{4\pi m} \Delta m_l \quad (11.13.7)$$

Applying the selection rule, the frequencies of the *three* lines are

$$\nu_1 = \nu_0 \quad (\Delta m_l = 0)$$

$$\nu_2 = \nu_0 + \frac{eB}{4\pi m} \quad (\Delta m_l = 1)$$

$$\nu_3 = \nu_0 - \frac{eB}{4\pi m} \quad (\Delta m_l = -1)$$

Consider the $2p \rightarrow 1s$ transition. The $2s$ -state for which $l = 0$, will not split, while the $2p$ -state, for which $l = 1$ will split into three with $m_l = +1, 0, -1$. This is illustrated in Fig. 11.12. The involved transitions are also marked.

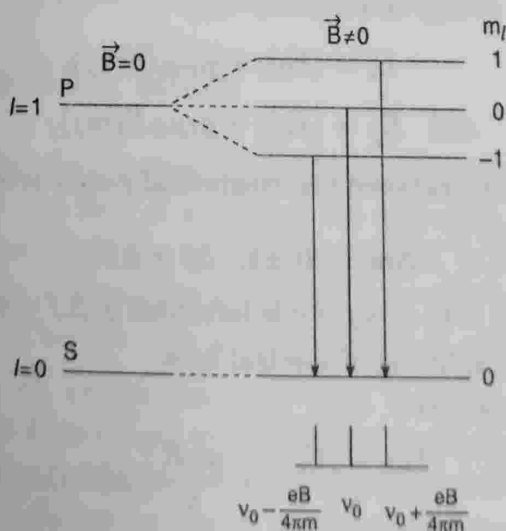


Fig. 11.12 Splitting of energy levels in a magnetic field for $l = 0$ and $l = 1$ states of an atom with only orbital angular momentum. Involved transitions are also marked

11.14 Anomalous Zeeman effect: Explanation

The splitting of spectral lines of atom with non-zero spin angular momentum in a fairly weak magnetic field shows, in general, to have a structure and is more complex than the normal Zeeman triplet. This phenomenon is the so-called *anomalous Zeeman effect*, although there is hardly any anomaly in it. It can be explained by considering the *electron spin*, in addition to the *orbital motion* of the electron.

Theory—Let the atom be placed in a magnetic field \vec{B} along z -axis. \vec{B} is relatively weak so that the coupling between \vec{L} and \vec{S} does not break down. In this case, therefore, the total angular momentum vector \vec{J} will precess about the magnetic field \vec{B} . The interaction energy of \vec{B} with the system is

$$\begin{aligned}\Delta E &= -\vec{\mu}_J \cdot \vec{B} = g \frac{e}{2m} \vec{J} \cdot \vec{B} \\ &= \frac{e}{2m} g J B \cos \theta, \text{ using (11.9.11)}\end{aligned}\quad (11.14.1)$$

where $\vec{\mu}_J$ is the total magnetic moment of the electron, g the Lande g -factor and θ the angle between \vec{B} and \vec{J} .

$$\therefore \Delta E = \frac{e}{2m} g B J_z = g \frac{e\hbar}{2m} B m_J = g \mu_B B m_J \quad (11.14.2)$$

$$(\because \cos \theta = J_z/J \text{ and } J_z = m_J \hbar)$$

$$\therefore \text{Energy of the state: } E = E_0 + \Delta E = E_0 + g \mu_B B m_J \quad (11.14.3)$$

The quantum number m_J can have the following $(2J + 1)$ -values:

$$m_J = -J, -J + 1, \dots, J - 1, J$$

So, we shall obtain $(2J + 1)$ equally spaced Zeeman sublevels. Consequently, each spectral line will split into a number of lines.

The initial and final energy states are:

$$E_i = (E_0)_i + g_i \mu_B B (m_J)_i \quad (11.14.4)$$

$$\text{and } E_f = (E_0)_f + g_f \mu_B B (m_J)_f \quad (11.14.5)$$

The possible transitions between the magnetically-split levels are governed by the following *selection rules*:

$$\Delta m_J = 0, \pm 1; \Delta l = \pm 1$$

$$m_J = 0 \rightarrow m_J = 0 \text{ is forbidden if } \Delta J = 0$$

and give rise to magnetic splitting of spectral lines.

The emitted frequencies are:

$$\begin{aligned}\nu &= \frac{E_i - E_f}{h} = \frac{(E_0)_i - (E_0)_f}{h} + \frac{\mu_B B}{h} [(g_i (m_J)_i - g_f (m_J)_f)] \\ &= \nu_0 + \frac{\mu_B B}{h} [(g_i (m_J)_i - g_f (m_J)_f)]\end{aligned}\quad (11.14.6)$$

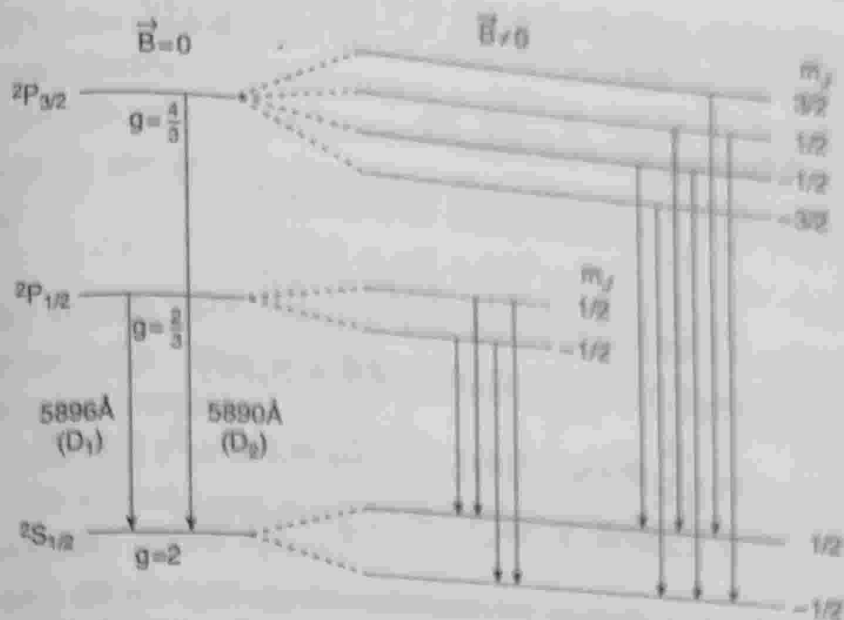


Fig. 11.13 Anomalous Zeeman effect: Zeeman splittings of D_1 and D_2 lines of sodium

Due to the presence of Landé g -factor in (11.14.2), the splitting of the levels is different for different multiplets. As a result, there are more spectral lines than the normal Zeeman triplet.

So, the **anomalous Zeeman pattern** appears as a direct effect of *electron spin*.

• The Zeeman splitting of D_1 and D_2 lines of sodium are shown in Fig. 11.13. The D_1 -line (transition ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$) and the D_2 -line (transition ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$) split into 4 and 6 lines respectively.

• For elements for which the ground states are 1S_0 , the spectral lines split even in weak field into *three* components only (normal Zeeman effect). For in these cases $S = 0$ and $J = L$ so that $g = 1$, implying that the upper and the lower states have the same splittings, independent of L and J . Examples: Mg, Ca, Sr, Cd etc.

11.15 Paschen-Back effect

The anomalous Zeeman effect is observed only when the magnetic field \vec{B} is relatively weak. When, however, the field \vec{B} is intense, the spin-orbit splitting would be small compared to the magnetic splitting of energy levels and, to a first approximation, can be neglected. The pattern of splitting of spectral lines then becomes similar to that of *normal Zeeman effect*. This is known as **Paschen-Back effect**.

Explanation—In an intense magnetic field, the spin-orbit coupling tends to breakdown, the vectors \vec{L} and \vec{S} get uncoupled and the vector \vec{J} ceases to exist. Then \vec{L} and \vec{S} start precessing independently about \vec{B} . Hence the corresponding magnetic moment vectors $\vec{\mu}_L$ and $\vec{\mu}_S$ can be treated as precessing independently about the field. So, the interaction energy ΔE in the field \vec{B} is given by

$$\Delta E = -\vec{\mu}_L \cdot \vec{B} - \vec{\mu}_S \cdot \vec{B} \quad (11.15.1)$$

$$\text{But, } \mu_L = -\frac{e}{2m}\vec{L} \text{ and } \mu_S = -\frac{e}{m}\vec{S} = -\frac{e}{2m}2\vec{S}$$

$$\begin{aligned} \therefore \Delta E &= \frac{e}{2m}(\vec{L} \cdot \vec{B} + 2\vec{S} \cdot \vec{B}) \\ &= \frac{e}{2m}(LB \cos \widehat{LB} + 2SB \cos \widehat{SB}) \\ &= \frac{e}{2m}[LB(L_z/L) + 2SB(S_z/S)] \\ (\because \cos \widehat{LB} &= L_z/L \text{ and } \cos \widehat{SB} = S_z/S) \\ &= \frac{eh}{2m}B(m_l + 2m_s) \quad [\because L_z = m_l h, S_z = m_s h] \\ &= \mu_B B(m_l + 2m_s) \quad (\because \mu_B = eh/2m) \end{aligned}$$

(11.15.2)

\therefore The energy of the level, including *interaction energy*, is given by

$$\begin{aligned} E &= E_0 + \Delta E = E_0 + \mu_B B(m_l + 2m_s) \\ &= E_0 + \mu_B B(m_l \pm 1) \quad (\because m_s = \pm \frac{1}{2}) \\ &= E_0 + \mu_B B m_l \pm \mu_B B \end{aligned}$$

(11.15.3)

Thus, but for the additional *constant* term $\mu_B B$, the expression is that of *normal Zeeman effect* (Eq. 11.13.3) due to the orbital motion only. The additional constant term, due to spin, also gets cancelled in a transition from one state to another on applying the selection rule $\Delta m_l = 0, \pm 1$ and $\Delta m_s = 0$. As a result the pattern for strong magnetic field, called **Paschen-Back effect**, is a *triplet*, as observed in normal Zeeman effect.

• There exists however a *residual spin-orbit interaction* between \vec{L} and \vec{S} even in a strong magnetic field and has been neglected here. This residual interaction makes the splitting complicated in that *each line* may have a *fine structure*.

11.16 Stark effect (Qualitative)

The **Stark effect** refers to the splitting of spectral lines under the influence of a very *strong external electric field* and may thus be considered as the electric analogue of Zeeman effect.

This splitting was first demonstrated by Stark in 1913, and hence the name Stark effect, with Balmer series lines of H-atom where every line splits into a number of components when excited in a strong electric field $\sim 10^5$ V/cm. Viewed *perpendicular to the field*, some of the components are found to be *plane polarized* with electric vector *parallel* to the field and others polarized with electric vector *normal* to the field. Since Stark-splitting is *very small* even in strong fields of 10^3 – 10^6 V/cm, high resolution spectrometers are essential to observe the effect.

The *physical mechanism* behind it is the *polarization of the atom* by the external electric field. The induced electric dipole moment created by the polarization interacts with the external electric field and causes a shift in energy. It is essentially a *quantum phenomenon* and can only be understood quantum mechanically.

The interaction energy of a hydrogen-like atom in an electric field is given by an expression like

$$\Delta E = aE + bE^2 + cE^3 \quad (11.16.1)$$

where E is the electric field strength and the coefficients a, b, c have been calculated quantum mechanically. They are found to depend on quantum number n and some other new quantum numbers.

The first term in (11.16.1) involves E to the first power and is called the *first order Stark effect*, the second term involves E to the second power and is called the *second order or quadratic Stark effect* and so on.

In *quadratic Stark effect*, the splitting varies with the square of the electric field strength and it occurs in atoms that have no permanent dipole moment in the ground state. In an external field \vec{E} , the atoms get polarized and the induced electric dipole moment \vec{d} is proportional to \vec{E} . In the field \vec{E} , therefore, it has the potential energy

$$-\vec{d} \cdot \vec{E} \sim E^2$$

The quadratic Stark effect is thus related to the *electric polarizability* of atoms.

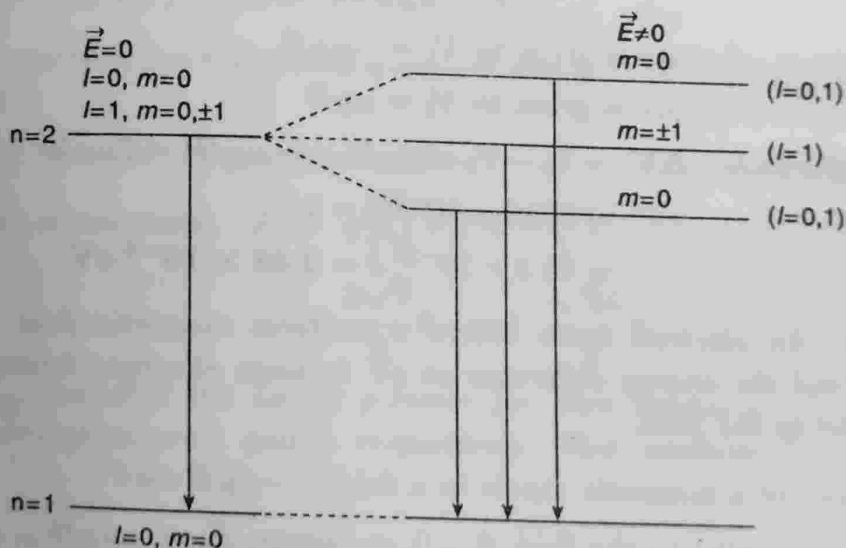


Fig. 11.14 Linear Stark effect in H-atom

Linear Stark effect occurs in H-atom and H-like atoms in which a degeneracy of states of equal principal quantum number n w.r.t orbital angular momentum arises, that is, states of different parity (e.g., $l = 0$ and $l = 1$) are mixed up (Fig. 11.14).

- Hydrogen in the ground state ($n = 1, l = 0$) does *not* display *linear Stark effect*.
- Measurement of Stark components provides an accurate method for the determination of dipole moment of atoms and molecules, an important electronic property.

11.17 Illustrated Examples

► **Example 1.** Show that for a given principal quantum number n , there are n^2 possible states of the atom.

Solution. Every combination of quantum numbers n, l and m_l defines a state of the atom. For a given n , the orbital quantum number l has the values

$$l = 0, 1, 2, \dots, (n-1)$$

For every l , again, there would be the following $(2l+1)$ values for the magnetic quantum number m_l .

$$m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

∴ Total number of possible states of the atom is given by

$$N(n, l, m_l) = \sum_{l=0}^{n-1} (2l+1) = 1 + 3 + 5 + \dots + (2n-1) = n^2.$$

► **Example 2.** An H-atom is placed in a magnetic field of 3 T. Compute the energy difference between $m_l = -1$ and $m_l = +1$ components in 2p state.

Solution. The interaction energy between the magnetic moment of electron and the magnetic field B is

$$V = \mu_B B m_l$$

∴ Energy of $m_l = -1$ -state is given by $V_1 = -\mu_B B$

Energy of $m_l = +1$ -state is given by $V_2 = \mu_B B$

∴ Energy difference, $\Delta V = V_2 - V_1 = \mu_B B - (-\mu_B B) = 2\mu_B B$

$$= 2(9.3 \times 10^{-24}) \times 3 \text{ J}$$

$$= 55.8 \times 10^{-24} \text{ J} = 3.48 \times 10^{-4} \text{ eV}$$

► **Example 3.** An electron beam enters a uniform magnetic field of flux density 1.2 Wb/m^2 . Find the energy difference in eV between electrons having spins parallel and anti-parallel to the field.

Solution. Energy of a magnetic dipole in a field $= -\mu_B B \cos \theta$

When spin is parallel to the field, $\theta = 0 \Rightarrow$ energy, $E_1 = -\mu_B B$

When spin is anti-parallel, $\theta = 180^\circ \Rightarrow$ energy, $E_2 = \mu_B B$

∴ Energy difference, $\Delta E = 2\mu_B B = 2 \times 9.3 \times 10^{-24} \times 1.2 \text{ J}$

$$= 13.95 \times 10^{-24} \text{ J} = 8.72 \times 10^{-5} \text{ eV}$$

► **Example 4.** An atomic state is denoted by $^4D_{5/2}$. Give the values of L, S and J . What should be the minimum number of electrons involved for this state? Give a possible electronic configuration.

Solution. Atomic state is ${}^4D_{5/2}$. So, $2S + 1 = 4 \Rightarrow S = 3/2$. D indicates $L = 2$ and $J = 5/2$ (the subscript).
 For each electron, $s = \frac{1}{2}$. So, the *minimum number of electrons* for $S = \frac{3}{2}$ is 3.
 Possible combinations for $L = 2$ with 3 electrons are:

$$l_1 = 0, l_2 = 0, l_3 = 2; l_1 = 0, l_2 = 1, l_3 = 1$$

Possible electronic configurations: s^2d^1 and s^1p^2 . The first configuration is rejected since the net spin = $\frac{1}{2}$. So, the *possible configuration* is s^1p^2 .

► **Example 5.** Find the precessional frequency of an electron orbit when placed in a magnetic field of 6 T.

Solution. The frequency $\Delta\nu_l$ of Larmor precession is given by

$$\Delta\nu_l = \frac{eB}{4\pi m}$$

Here, $B = 6 \text{ T} = 6 \text{ Wb/m}^2$, $e = 1.6 \times 10^{-19} \text{ C}$ and $m = 9.1 \times 10^{-31} \text{ kg}$.

$$\begin{aligned} \therefore \Delta\nu_l &= \frac{1.6 \times 10^{-19} \times 6}{4 \times 3.14 \times 9.1 \times 10^{-31}} \\ &= 8.4 \times 10^{10} \text{ Hz} \end{aligned}$$

► **Example 6.** Using the vector atom model, determine the possible values of the total angular momentum of an f -electron.

Solution. An f -electron has the orbital quantum number $l = 3$. Also, its spin quantum number $s = 1/2$.

\therefore Total angular momentum quantum number, $j = l \pm s = 3 \pm \frac{1}{2} = \frac{7}{2}, \frac{5}{2}$.

\therefore Total angular momentum, $J = \sqrt{j(j+1)}\hbar = \sqrt{\frac{7}{2} \times \frac{9}{2}}\hbar$ and $\sqrt{\frac{5}{2} \times \frac{7}{2}}\hbar$

$$= \frac{3\sqrt{7}}{2}\hbar \text{ and } \frac{\sqrt{35}}{2}\hbar.$$

► **Example 7.** Show that the Lande g -factor for pure orbital momentum and pure spin angular momentum are 1 and 2, respectively. Also, evaluate the g -factor for the 3P_1 -state.

Solution. Pure orbital angular momentum implies $\vec{S} = 0$.

$$\text{So, } \vec{J} = \vec{L} + \vec{S} = \vec{L}.$$

$$\therefore g = 1 + \frac{L(L+1) - L(L+1)}{2L(L+1)} = 1$$

Pure spin angular momentum implies $\vec{L} = 0$. So, $J = \vec{S}$

$$\therefore g = 1 + \frac{S(S+1) + S(S+1)}{2S(S+1)} = 2.$$

For 3P_1 -state, $2S + 1 = 3 \Rightarrow S = 1$; P implies $L = 1$ and $J = 1$ (subscript).

$$\therefore g = 1 + \frac{(1 \times 2) + (1 \times 2) - (1 \times 2)}{2(1 \times 2)} = 1 + \frac{1}{2} = \frac{3}{2}$$

► **Example 8.** An element, on being excited, is placed in a magnetic field of 0.5 T. Calculate the wavelength-shift in the spectral line of 6000 Å. Assume normal Zeeman splitting.

Solution. From the relation of frequency-shift, we have

$$\Delta\nu = \frac{eB}{4\pi m}$$

Since $\nu = c/\lambda$, $d\nu = -cd\lambda/\lambda^2$. So, $\Delta\lambda = \lambda^2\Delta\nu/c$, save the sign.

$$\begin{aligned} \therefore \text{Wavelength shift, } \Delta\lambda &= \frac{\lambda^2 eB}{4\pi mc} = \frac{(6 \times 10^{-7})^2 \times (1.6 \times 10^{-19}) \times 0.5}{4 \times 3.14 \times (9.1 \times 10^{-31}) \times (3 \times 10^8)} \text{ m} \\ &= 0.0839 \times 10^{-10} \text{ m} = \mathbf{0.0839 \text{ \AA}} \end{aligned}$$

► **Example 9.** Calculate the Lande g -factor and the total magnetic moment for the following atomic states: (a) $^2S_{1/2}$ and (b) $^2P_{1/2}$.

Solution. (a) For $^2S_{1/2}$ state, $l = 0$, $j = \frac{1}{2}$ and $2s + 1 = 2 \Rightarrow s = 1/2$.

$$\begin{aligned} \therefore \text{Lande } g\text{-factor, } g &= 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \\ &= 1 + \frac{\frac{1}{2} \left(\frac{3}{2} \right) + \frac{1}{2} \left(\frac{3}{2} \right) - 0 \times 1}{2 \times \frac{1}{2} \times \frac{3}{2}} \\ &= 1 + \frac{\frac{3}{4} + \frac{3}{4}}{\frac{3}{2}} = 1 + 1 = \mathbf{2} \end{aligned}$$

$$\begin{aligned} \therefore \text{Total magnetic moment, } \mu_j &= g\sqrt{j(j+1)}\mu_B \\ &= 2\sqrt{\frac{1}{2} \times \frac{3}{2}}\mu_B \\ &= \mathbf{\sqrt{3}\mu_B} \end{aligned}$$

(b) For the $^2P_{1/2}$ -state, we have, $l = 1$, $j = \frac{1}{2}$, $s = \frac{1}{2}$.

$$\therefore \text{Lande } g\text{-factor, } g = 1 + \frac{\frac{1}{2} \times \frac{3}{2} + \frac{1}{2} \times \frac{3}{2} - 1 \times 2}{2 \times \frac{1}{2} \times \frac{3}{2}} = 1 - \frac{1}{3} = \frac{2}{3}$$

$$\text{Total magnetic moment, } \mu_j = \frac{2}{3}\sqrt{\frac{1}{2} \times \frac{3}{2}}\mu_B = \frac{1}{\sqrt{3}}\mu_B$$

► **Example 10.** A spectrometer can resolve spectral lines in the region $\lambda \approx 6000 \text{ \AA}$, when separated by $\Delta\lambda = 0.1 \text{ \AA}$. Find the value of the external magnetic field required to confirm the normal Zeeman triplet.

Solution. The energy-separation ΔE between two consecutive spectral lines is

$$\Delta E = \mu_B B \quad (11.17.1)$$

where B is the external magnetic field.

\therefore Frequency-separation $\Delta\nu$ between them is

$$\Delta\nu = \mu_B B/h \quad (11.17.2)$$

But, $\Delta\nu = \Delta \left(\frac{c}{\lambda} \right) = \frac{c\Delta\lambda}{\lambda^2}$, save the sign. (11.17.3)

From (11.17.2) and (11.17.3), the **magnetic field** is given by

$$B = \frac{hc \cdot \Delta\lambda}{\mu_B \lambda^2} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8 \times 0.1 \times 10^{-10}}{9.3 \times 10^{-24} \times (6.0 \times 10^{-7})^2} \\ = 0.593 \text{ Wb/m}^2$$

► **Example 11.** Draw the Zeeman splittings of the D_2 and D_1 lines of sodium corresponding to transitions from the excited states $3^2P_{3/2}$ and $3^2P_{1/2}$ to the ground state $3^2S_{1/2}$.

Solution. For $3^2S_{1/2}$ level, $J = \frac{1}{2}$. So, it splits into two levels for which $m_J = \frac{1}{2}$ and $-\frac{1}{2}$.

For $3^2P_{1/2}$ level, $J = \frac{1}{2}$. So, it also splits into two levels, for which $m_J = \frac{1}{2}, -\frac{1}{2}$.

For $3^2P_{3/2}$ level, $J = \frac{3}{2}$. So, it splits into four levels for which $m_J = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$.

So, the D_1 line which is singlet in field-free condition, splits into **four Zeeman lines** and D_2 line into **six Zeeman lines**.

The splitting and the allowed transitions are illustrated in Fig. 11.13.

► **Example 12.** In a Stern-Gerlach type experiment, the magnetic field varies with distance in z -direction according to $dB_z/dz = 1.4 \text{ T/mm}$. Silver atoms travel a distance $z = 3.5 \text{ cm}$ through the magnet. The speed of atoms emerging from oven is $v = 750 \text{ m/s}$. Find the separation of the two beams as they leave the magnet. Mass of silver atom $= 1.8 \times 10^{-25} \text{ kg}$ and its magnetic moment is 1 Bohr magneton ($= 9.27 \times 10^{-24} \text{ J/T}$).

Solution. Potential energy of the atom in the magnetic field is

$$V = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z \quad (\because \text{Field has only } z\text{-component})$$

\therefore Force on the atom,

$$F_z = -\frac{dV}{dz} = \mu_z \frac{dB_z}{dz}$$

∴ Acceleration of a silver atom in passing through the magnet is

$$a = \frac{F_z}{m} = \frac{\mu_z (dB_z/dz)}{m}$$

where m is the mass of the silver atom.

∴ Vertical deflection Δz of either beam is $\Delta z = \frac{1}{2}at^2$, where t = time to traverse inside the field = x/v . So, the separation d of the beams as they leave the magnet is

$$\begin{aligned} d &= 2\Delta z = at^2 = \frac{\mu_z (dB_z/dz)x^2}{mv^2} \\ &= \frac{(9.27 \times 10^{-24} \text{ J/T}) \times (1.4 \times 10^3 \text{ T/m}) \times (3.5 \times 10^{-2} \text{ m})^2}{(1.8 \times 10^{-25} \text{ kg}) \times (750 \text{ m/s})^2} \\ &= 1.6 \times 10^{-4} \text{ m} = 0.16 \text{ nm} \end{aligned}$$

Review Questions

- (a) Describe the essential elements that characterize the vector atom model. Discuss the various quantum numbers associated with the model.
(b) Show that the magnetic moment of an orbiting electron is given by

$$\vec{\mu}_l = -\frac{e}{2m} \vec{L}$$

with usual meanings of the symbols.

- Discuss diagrammatically the two possible ways in which the vectors \vec{L} and \vec{S} combine to form the vector \vec{J} . Why do \vec{L} and \vec{S} precess around \vec{J} ?
- Show that the total magnetic moment of an orbital electron in the state with total angular momentum \vec{J} is given by $\mu_J = -\mu_B J/\hbar$.
Write the expression for the Lande g -factor.
- Explain the origin of the total quantum number j on the basis of spin-orbit interaction. Discuss the selection rules for l and j .
Explain the origin of sodium D -lines.
- Explain the origin of normal Zeeman effect. What is Larmor's frequency?
- A source of light is placed between the poles of an electromagnet. What will you observe if the light is examined by a spectroscope in directions parallel and perpendicular to the magnetic field. Assume the magnetic field to be not too strong. Give an explanation of the phenomenon.

(Calcutta Hons.)

7. Describe, in details, a theory which explains the anomalous Zeeman effect. Illustrate, with diagrams, the Zeeman splitting of sodium D_1 and D_2 lines. Why is the anomalous effect, more commonly observed than normal Zeeman effect?
8. Describe an arrangement for demonstrating that spectral lines are split up when the source is placed in a strong magnetic field. Describe the nature of splitting generally observed.
(Calcutta Hons.)
9. Explain the splitting of atomic spectral lines in presence of moderate magnetic field by taking electron spin into account and hence explain the splitting of ($2P_{3/2} \rightarrow 1S_{1/2}$) and ($2P_{3/2} \rightarrow 1S_{1/2}$) line of hydrogen spectrum in a moderate magnetic field.
10. What is normal Zeeman effect? Discuss in detail how it is explained using quantum theory. Derive the expression for the frequency-shift.
11. What is Paschen-Back effect? Why is there no spin-orbit coupling for the ground state of hydrogen?
12. Apply the space quantization principle to determine the values of J for the following values of L and S vectors: $L_1 = 1, S = 1; L = 2, S = 1; L = 1, S = 3/2; L = 2, S = 3/2$.
13. Describe Stern-Gerlach's experiment of studying the atomic rays in a non-homogeneous magnetic field and discuss in full what the experimental results establish.
14. Apply the space quantization principle to determine the values of J for the following values of L and S vectors: $L = 1, S = 1; L = 2, S = 1; L = 1, S = 3/2; L = 2, S = 3/2$.

Short and Objective Questions

1. Explain gyromagnetic ratio and Bohr magneton. Show that the spin magnetic moment of electron is equal to Bohr magneton.
2. What is Larmor's precession? Define Larmor frequency. The angular momentum vector \vec{L} never points in the z -direction. Why?
3. Define gyromagnetic ratio and state the relation connecting $\vec{\mu}_s$ and \vec{S} in terms of gyromagnetic ratio.
4. What is normal Zeeman effect? Distinguish between normal and anomalous Zeeman effect. Show, with a diagram, what will you observe in longitudinal and transverse views of normal Zeeman effect?
5. What is Lande g -factor? Use it to illustrate the anomalous magnetic splitting of D -lines of sodium.
6. What is Paschen-Back effect? Why is there no spin-orbit coupling for the ground state of hydrogen?

7. Indicate which of the following four transitions are allowed? If forbidden, state the rule that is being violated?
 (a) $4p \rightarrow 3p$, (b) $3d \rightarrow 2d$, (c) $2p \rightarrow 1s$, (d) $4d \rightarrow 3s$.
8. The minimum value of angular momentum by coupling three angular momenta 1, $3/2$ and $5/2$ is
 (a) -5 , (b) $1/2$, (c) 0 , (d) 1 .
9. The energy levels of a multi-electron atom depend on
 (a) n , (b) l , (c) both n and l , (d) none.
10. The number of allowed orientations of spin angular momentum of the electron in H-atom is
 (a) 0, (b) 1, (c) 2, (d) 3.
11. The value of Lande g -factor for s -state is
 (a) 0, (b) 1, (c) 2, (d) $\frac{1}{2}$.
12. The number of values allowed to quantum number j of electron in the H-atom for a given non-zero l is
 (a) 0, (b) 1, (c) 2, (d) 3.
13. The n and l values of the last electron in the sub-shell of ^{17}Cl are
 (a) $n = 2, l = 1$, (b) $n = 3, l = 0$, (c) $n = 3, l = 1$, (d) none.
14. If elements with $n > 4$ were not allowed in nature, the number of possible elements would have been
 (a) 60, (b) 32, (c) 4, (d) 64.

[Hints. $2 \times 1^2 + 2 \times 2^2 + 2 \times 3^2 + 2 \times 4^2 = 2 + 8 + 18 + 32 = 60$]

Problems

- Calculate the numerical value of Bohr magneton. Use the values of the fundamental constants from memory. [$9.27 \times 10^{-24} \text{ J/T}$]
- A 15 kV electron circulates at right angles to a uniform magnetic field of 0.2 Wb/m^2 . Calculate the magnetic dipole moment produced by it. [$1.2 \times 10^{-4} \text{ Am}^2$]
- Calculate the value of the energy and the angular momentum of an electron in an H-atom in the $3p$ and $4p$ states respectively. [$1.51 \text{ eV}, 1.4 \times 10^{-34} \text{ Js}; 0.85 \text{ eV}, 1.48 \times 10^{-34} \text{ Js}$]

4. Find the maximum potential energy associated with the magnetic dipole moment of a $4p$ electron in an external magnetic field of 0.25 Wb/m^2 . [$2.05 \times 10^{-6} \text{ eV}$]
5. A beam of electron enters a uniform magnetic field of flux density 1.2 Wb/m^2 . Find the energy difference between the electrons whose spins are parallel and anti-parallel to the field. [$1.39 \times 10^{-4} \text{ eV}$]
6. If atoms could contain electrons with principal quantum number up to and including $n = 6$, how many elements would be there? (Dacca Hons.) [182]
7. The component of magnetic dipole moment μ_l along the z -axis is given by $(\mu_l)_z = \mu_B m_l$, i.e., the z -components of μ_l are integral multiples of Bohr magneton. Hence μ_B is a natural unit for the determination of $(\mu_l)_z$. How many values for $(\mu_l)_z$ are possible for $n = 3$? Is μ_l space-quantized? How many orientations of μ_l are possible for the d -state? [5, Yes, 5]
8. Calculate the precession frequency of a proton in a magnetic field of 0.5 Wb/m^2 . Given that the magnetic moment and quantized spin angular momentum of a proton are $1.4 \times 10^{-26} \text{ Am}^2$ and $0.53 \times 10^{-34} \text{ Js}$ respectively. [$2.1 \times 10^7 \text{ Hz}$]
9. The ground state of chlorine is $^2P_{3/2}$. Find its magnetic moment. Into how many substrates will the ground state split in a weak magnetic field? [$5\mu_B, 3$]
10. A 5 eV proton circulates at right angles to a uniform magnetic field of 0.0063 tesla . Determine the magnetic dipole moment produced by the proton. How many magneton is this? [$0.126 \text{ Am}^2, 1.4 \times 10^{22}$]
11. An H-atom is placed in an intense magnetic field of 0.8 T . What is the separation between two consecutive states when $\lambda = 5000 \text{ \AA}$? Assume that the magnetic field produces normal Zeeman triplet. [0.0941 \AA]
12. A sample of certain element is placed in a magnetic field of flux density 0.3 Wb/m^2 . How far apart are the Zeeman components of a spectral line of 4500 \AA ? [0.0283]
13. With a flux density 1.2 Wb/m^2 , a spectral line of wavelength 6000 \AA shows a separation of 0.40 \AA between the component lines in the normal longitudinal Zeeman effect. What is the value of e/m_0 for the electron? [$1.67 \times 10^{11} \text{ C/kg}$]
14. Find the values of L, S and J and determine the possible angles between \vec{L} and \vec{S} , for d -electron of H-atom. [$\sqrt{6}\hbar; \sqrt{3}\hbar/2; \sqrt{35}\hbar/2, \sqrt{15}\hbar/2; 61.87^\circ, 135^\circ$]
15. (a) Determine the lengths of angular momentum vectors that represent the orbital motion of an electron in a state with $l = 1$ and in a state $l = 2$. [$\sqrt{2}\hbar$ for $l = 1, \sqrt{6}\hbar$ for $l = 2$]
 (b) What are the possible z -components of vector \vec{L} which represents the orbital angular momentum of a state with $l = 2$? [$\sqrt{2}\hbar, \hbar, 0, -\hbar, -\sqrt{2}\hbar$]

16. Two energy levels, one corresponding to $m_s = \frac{1}{2}$ and the other $m_s = -\frac{1}{2}$, result when an electron of magnetic moment μ_s is placed in a magnetic field \vec{B} . Show that the energy separation between the two states is $2\mu_B$.
17. Calculate the angles between the orbital angular momentum vector \vec{p}_l and an applied magnetic field for $l = 1, 2$ and 3 ? For different l , what are the maximum values of the components of \vec{p}_l along the magnetic field? Determine the ratios of these components and the magnitude of \vec{p}_l in each case.
18. Determine the Lande g -factor and the total magnetic moment for the states $^2P_{3/2}$ and $^2D_{3/2}$.
[$\frac{4}{3}, \frac{2}{3}\sqrt{15}\mu_B$; $\frac{4}{5}, \frac{2}{5}\sqrt{15}\mu_B$ for the states]
19. Calculate Larmor's precessional frequency ν_L for $B = 1$ T. Hence calculate the energy difference between the consecutive sublevels caused by magnetic splitting of an atomic energy level. Neglect the spin of the electron.
[1.4×10^{10} Hz, 5.8×10^{-5} eV]
20. In a Stern-Gerlach experiment with silver, the following data were obtained:
length of magnetic field = 0.04 m
distance of screen from mid-point of field = 0.12 m
initial speed of silver atoms = 500 ms⁻¹
rate of variation of flux density = 1.5 T mm⁻¹
maximum separation between two traces = 3 mm.

Compute the value of the magnetic moment of silver atom in the direction of the magnetic field.
[9.33×10^{-24} J/T]

21. A beam of silver atoms (mass of silver atom = 107.868 amu) moving with a velocity of 10^5 cm/s passes through a magnetic field of gradient 0.5 Wb/m²/cm for a distance of 10 cm. Calculate the separation between the two components of the beam as it comes out of the magnetic field.
[2.6 mm]

[Hints. Please consult Illustrated Ex. 12. Utilize the formula

$$d = \frac{\mu_z (dB_z/dz) x^2}{mv^2} \quad \text{proved therein}]$$

22. In a Stern-Gerlach experiment, the gradient of the magnetic field is 5 volt.s.m⁻² with pole pieces 0.07 m long. A narrow beam of silver atoms from an oven at 1250 K passes through the magnetic field. Calculate the separation of the beams as they emerge from the magnetic field.
[6.5×10^{-3} m]

23. A dipole of moment $\vec{\mu}$ is placed in a magnetic field \vec{B} . Show that the interaction energy of magnetic moment in the field is given by $\vec{\mu} \cdot \vec{B}$.

[Hints. The dipole will experience a torque τ in the magnetic field, given by

$$\hat{\tau} = \vec{\mu} \times \vec{B} = \mu B \sin \theta$$

θ being the angle made by $\vec{\mu}$ with \vec{B} (Fig. 11.7).

The torque will tend to rotate the dipole in the field direction. The energy-change ΔE that would result from this rotation is in the form potential energy.

Conventionally, ΔE is taken to be zero where it is aligned at right angles to \vec{B} . So, to compute ΔE at any angle θ , we are to find the amount of work to be done to rotate the dipole from $\theta = 90$ to $\theta = \theta$. This is

$$\Delta E = \int_{\pi/2}^{\theta} \tau d\theta = \int_{\pi/2}^{\theta} \mu B \sin \theta d\theta = -\mu B \cos \theta = -\vec{\mu} \cdot \vec{B}$$

24. Find the values of L and S of the ground state of nitrogen.

[Hints. Electronic configuration of nitrogen is $1s^2 2s^2 2p^3$. So, the possible values of $M_s = 3/2$. To maximize M_L , we assign the maximum value of $m_l = 4$ to the first electron, the maximum value of m_l left for second electron is zero and that left for the third is -1

$$\therefore M_{L,\max} = 1 + 0 + (-1) = 0 \Rightarrow L = 0.$$

For the ground state of nitrogen, $L = 0, S = 3/2$.]